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Bench and Pilot Scale Process Evaluation of Reburning for In-Furnace NOx Reduction

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16. ABSTRACT The paper describes a combined experimental and theoretical study, undertaken to quantify the impact of fuel and process parameters on reburning effectiveness and provide the scaling information required for commercial application of reburning under highly varied industrial conditions. All work, under both 25 kW and 3.0 MW scales, focused on the importance and the fate of the reactive nitrogen species in the reburning zone. Study results confirm the potential of reburning for significant NOx reductions, but also demonstrate that a constant reburning effectiveness cannot be assumed under all conditions. The NOx reduction possible through reburning depends primarily on: the NO concentration at the end of the primary zone; the stoichiometry, temperature, and residence time in the fuel-rich reburning zone; the mixing and stoichiometry of the reburning fuel jet; and the temperature in the final burnout zone. At the optimum reburning stoichiometry (SR2 = 0.9) the exhaust emissions correlate linearly with the sum of the primary NOx and the equivalent reburning fuel nitrogen. Optimum effectiveness requires adequate primary zone residence time to ensure complete combustion of the primary fuel. Reburning zone residence times of at least 400 ms are desirable, and high temperatures favor molecular nitrogen formation.

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BENCH AND PILOT SCALE PROCESS EVALUATION OF REBURNING FOR IN-FURNACE NO_x REDUCTION

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This paper describes a combined experimental and theoretical study which was undertaken to quantify the impact of fuel and process parameters on reburning effectiveness and provide the scaling information required for commercial application of reburning under highly varied industrial conditions. Initially parametric screening studies were conducted in a 25 KW refractory-lined tunnel furnace. These studies were supported by large scale testing in a 3.0 MW pilot scale facility. The work at both scales focused on the importance and the fate of the reactive nitrogen species within the reburning zone.

The results of this study confirm the potential of the reburning process for significant NO_x reductions, but they also demonstrate that a constant reburning effectiveness cannot be assumed under all conditions. The NO_x reduction possible through reburning depends primarily on the NO concentration at the end of the primary zone; the stoichiometry, temperature, and residence time in the fuel-rich reburning zone; the mixing and stoichiometry of the reburning fuel jet; and the temperature in the final burnout zone. At the optimum reburning stoichiometry ($SR_2 = 0.9$) the exhaust emissions correlate linearly with the sum of the primary NO_x and the equivalent reburning fuel nitrogen. Optimum effectiveness requires adequate primary zone residence time to insure complete combustion of the primary fuel. Reburning zone residence times of at least 400 ms are desirable and high temperatures favor molecular nitrogen formation. Rapid mixing of the reburning fuel enhances the effectiveness of the NO_x destruction process but it can potentially detract from the overall process efficiency with coal reburning due to increased conversion of reburning fuel nitrogen unless the fuel is transported with an essentially inert gas stream. Extremely low exhaust emission levels can be achieved with coal reburning if the final burnout zone can be operated at a temperature low enough to promote in-situ thermal de-NO_x.

Introduction

Reburning is a combustion modification technology which removes NO_x from combustion products by using fuel as the reducing agent. This technology, which is alternately referred to as "in-furnace NO_x reduction" or "staged fuel injection", has been found to involve kinetic processes similar to those in staged combustion. The concept was originally developed by the John Zinc Company[1] and Wendt et al.[2] based on the principle of Myerson et al.[3] that CH fragments can react with NO. More recently several investigators have conducted detailed investigations of the process[4–9] and demonstrated its potential for large scale applications.[5,4,10,11]

Conceptually the reburning process can be divided into three zones:

- *Primary Zone:* This main heat release zone accounts for approximately 80% of the total heat input to the system and is operated under fuel-lean conditions. The level of NO_x exiting this zone is defined to be the input to the reburning process.
- *Reburning Zone:* The reburning fuel (normally 10 to 20% of the total fuel) is injected downstream of the primary zone to create a fuel-rich, NO_x reduction zone. Reactive nitrogen enters this zone from two sources: the primary NO_x and the fuel nitrogen in the reburning fuel. These reactive nitrogen species react with hydrocarbon fragments from the reburning fuel to produce intermediate species NH_3 and HCN.[3–5,8] Additionally some nitrogen is converted to N_2 and some is retained as NO. If the reburning fuel is a solid, nitrogen may also leave this zone as char nitrogen.[5]
- *Burnout Zone:* In this final zone, air is added to produce overall lean conditions and oxidize all remaining fuel fragments. The total

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fixed nitrogen species (TFN = NH_3 + HCN + NO + *Char* N) will either be oxidized to NO_x or reduced to molecular nitrogen.

This paper summarizes the results of a study which was undertaken to quantify the impact of fuel and process parameters on reburning effectiveness and provide the scaling information required for commercial application of the process under highly varied industrial conditions. Initially parametric screening studies were conducted in a 25 KW refractory-lined tunnel furnace. These studies were subsequently supported with testing in a 3.0 MW pilot scale facility and with finite rate kinetic modeling. The work at both scales focused on the importance and the fate of the reactive nitrogen species within the reburning zone. The experimental conditions were designed to directly simulate the 400–700 ms residence time available in a practical boiler between the burner zone and superheater tubes. Boiler heat transfer calculations suggest that the reburning fuel must be injected at 1400 ± 50C and the reburning air at 1300 ± 50 C to insure complete burnout prior to the superheater.

Experimental Systems

The process studies were conducted in the 2.5 m refractory-lined controlled temperature tower (CTT). This 25 KW furnace (Fig.1) is 20.3 cm in diameter and the time/temperature profile can be adjusted using backfired heating sections within the refractory walls.[12] The primary fuels were fired at 17.6 KW using two types of burners: a premixed burner for the gaseous fuel (propane) and pulverized coals, and a diffusion burner with twin fluid atomization for liquid fuels (oil and coal-water slurry).

The reburning fuels were injected immediately downstream of a refractory choke with a 90° injector located at the centerline of the furnace. This injector allowed the reburning fuel, transported with nitrogen, to flow radially outward through four 0.5 cm holes and mix rapidly with the oncoming primary effluent. Another refractory choke was inserted downstream to isolate the fuel rich reburning zone from the final burnout zone. Burnout air was also injected radially.

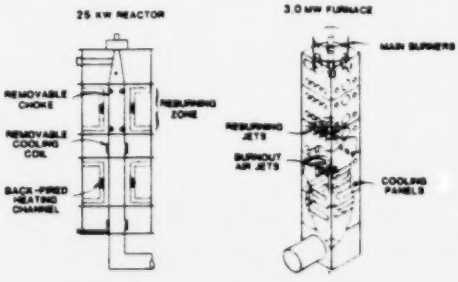

FIG. 1. Schematics of Bench and Pilot Scale Furnaces

The 3.0 *MW*, down-fired tower furnace (Fig. 1) used in the pilot-scale investigations was refractory-lined and water-jacketed with inside dimensions of 1.2 × 1.2 × 8.0 m. The four main diffusion burners each consisted of an inner pipe for axial primary fuel injection and an outer pipe, equipped with swirl vanes, for the main combustion air. This four burner array produced relatively uniform velocity and composition profiles at the primary zone exit.[13]

The furnace contained seven rows of ports for reburning fuel and burnout air injection. The temperature profile was manipulated by insertion of cooling panels, positioned against the furnace walls. The reburning fuel and burnout air injectors were designed to maintain jet mixing similarity between the pilot-scale furnace and a full scale boiler[14] based on empirical correlations for entrainment rate[15] and jet penetration.[16]

Exhaust gas samples were withdrawn through a stainless steel, water-jacketed probe and analyzed for NO_x (chemiluminescence), O_2 (paramagnetic), CO/CO_2 (NDIR), and SO_2 (NDUV). Furnace thermal profiles were characterized with a suction pyrometer.

The fuels used in this study included natural gas (containing 90% CH_4, 6% C_2H_6 and 1% C_3H_8 by volume), propane, a low nitrogen (0.2%) Middle East residual oil, a high nitrogen (0.8%) residual oil from Kern County, California, a Yallourn predried Australian brown coal, a Beulah, N.D. lignite, a subbituminous coal from Colstrip, Montana, a Utah high volatile bituminous coal and a medium volatile bituminous coal from Rosa, Alabama. In addition, non-hydrocarbon fuels, hydrogen and CO, were used as reburning fuels and a coal-water slurry, which contained 30% water, was used as a primary fuel. Complete analyses of the oils and coals are available in the literature.[12,17]

Process Parameters

Available Reactive Nitrogen

Figure 2 compares the effectiveness of different reburning fuels as the reburning zone stoichiometry (SR_2) was reduced from 1.1 (no

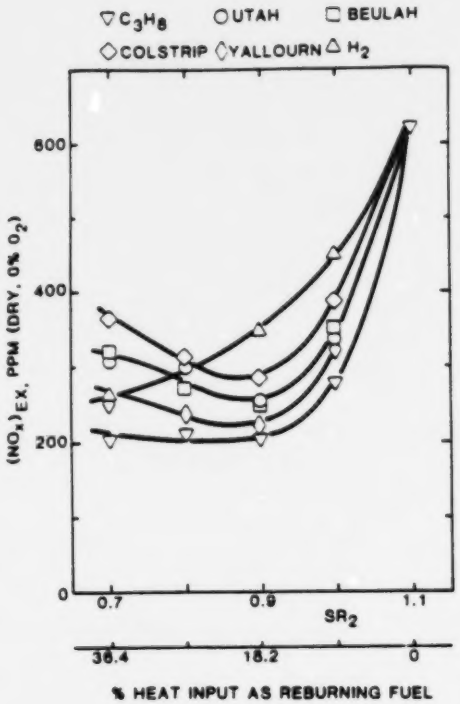

FIG. 2. Influence of Reburning Zone Stoichiometry on Exhaust Emissions for Various Reburning Fuels (Propane primary, $(NO_x)_P$ = 630 ppm, τ_2 = 400 ms, reburning fuel transport: N_2)

reburning) to 0.7 (ca. 36% reburning fuel). In these studies the primary zone NO_x, $(NO_x)_p$ was 630 ppm and the primary zone stoichiometric ratio (SR_1) was 1.1. Propane and natural gas (not shown) are the most effective reburning fuels; hydrogen and CO (not shown) are the least. The hydrocarbon fuels rapidly form CH fragments which convert the primary NO_x to HCN while CO and H_2 only form CH fragments through interactions with H_2O or CO_2 species. Detailed measurements at the end of the reburning zone indicated that HCN formation was significantly less with hydrogen or CO as the reburning fuel. The coals are also effective at reducing the NO_x from the primary zone; however, they are less effective than propane because they add additional reactive fuel nitrogen. All of the hydrocarbon fuels exhibited an optimum stoichiometry at SR_2 = 0.9 because of a trade-off between the efficiency of primary NO_x destruction and the formation of HCN. The fact that both propane and the solid fuels have the same optimum rich

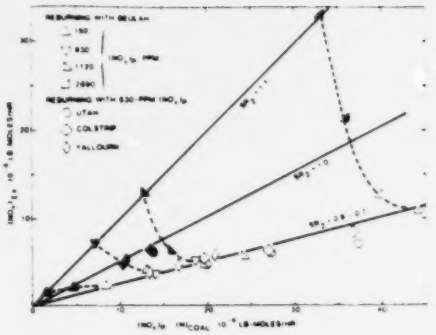

FIG. 3. Correlation of Exhaust NO_x with Primary NO_x + Equivalent Reburning Fuel Nitrogen

zone stoichiometry suggests that fuel volatility is not of first order importance (so long as the rich zone residence time and stoichiometry are adequate to insure overall, fuel-rich conditions).

The difference in the minimum NO_x levels achieved are directly related to differences in the fuel nitrogen contents of the various hydrocarbon fuels as illustrated in Fig. 3. Here the exhaust NO_x emissions are plotted on a molar basis as a function of the total available reactive nitrogen (primary zone NO_x plus fuel nitrogen in the reburning coal) for all of the stoichiometries and fuels shown in Fig. 2. In addition data from tests with various primary NO_x levels have been added. Applications of reburning causes the emissions to fall onto operating lines where the source of the reactive nitrogen becomes indistinguishable; at SR_2 = 0.9 primary zone NO_x and reburning fuel nitrogen are equivalent in terms of their impact on exhaust NO_x emissions. Thus, in systems with already low primary emissions (less than 600 ppm) reburning fuel nitrogen can become very significant.[7] (The nitrogen associated with reburning using 20% Utah coal at 1.5% fuel nitrogen is equivalent to 780 ppm of primary NO_x.)

The slope of the operating line under these baseline conditions corresponds to 25% conversion of the total available nitrogen. Figure 3 indicates that this slope is not strongly dependent on reburning fuel type; however, it does depend on the combustion conditions as will be discussed in the following sections.

Figure 4 summarizes data from a test sequence in which propane, three coals, two oils, and a coal-water slurry were alternately used as the primary fuel; the reburning fuel was always natural gas. (These experiments are the reverse of those shown in Fig. 3 where the primary fuel was always gas and the reburning fuel was

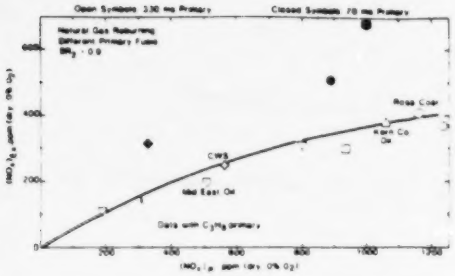

FIG. 4. Impact of Primary NO_x and Primary Residence Time with Nitrogen-Free Reburning Fuel

varied.) In this case the data can be simply correlated in terms of primary NO_x because it is identically equal to the total available reactive nitrogen; the natural gas reburning fuel contains no reactive nitrogen. Thus these experiments allow the primary NO_x and the reburning fuel nitrogen effects to be decoupled. The data from the wide spectrum of primary fuels correlate well with the solid line (doped propane primary) again indicating that the total available reactive nitrogen is the only composition variable of major importance under normal operating conditions.

In the summary the reactive nitrogen studies indicate that the reburning zone stoichiometry should be fuel-rich to achieve optimum emissions reductions. If the reburning fuel is nitrogen free, stoichiometries ≤ 0.9 are essentially equal in effectiveness; with heavy oils and coals $SR_2 = 0.9$ is an optimum stoichiometry because further decreases in SR_2 add additional reactive nitrogen through the reburning fuel and result in higher exhaust NO_x emissions. Under optimized reburning conditions exhaust NO_x is directly related to the sum of the primary NO_x and the reburning fuel nitrogen and the two nitrogen sources are essentially equivalent in terms of conversion to exhaust NO_x. Thus, if the initial NO_x emissions are very low (e.g. 100 ppm) reburning with a high nitrogen coal can actually increase exhaust NO_x.

System Parameters

This section of the paper focuses on the bench scale studies conducted to optimize the system design parameters, specifically the location of the reburning fuel injection, the location of the final burnout air injection and the optimum thermal environment.

Figure 4 also shows data which were obtained with a short primary residence time (70 ms). Here the reburning fuel was injected close to the main burner to establish the impact of overlapping zones in practical systems where inadequate total residence time is available prior to the convective passages. (The final burnout air injection was also moved correspondingly to maintain the 400 ms rich zone residence time in each experiment.) In principle reducing the primary zone residence time should help reburning effectiveness because it increases the rich zone temperature: however, these data indicate that with all of the coals tested (including the coal-water slurry) decreasing the primary zone residence time from 330 ms to 70 ms had a significant detrimental impact on the effectiveness of the reburning concept. Internal measurements indicated that this was primarily because the effective reburning zone stoichiometry (SR_2) was significantly increased due to incomplete commbustion in the primary zone. The oxygen concentration at the primary exit was 6% with the Rosa coal and 9% with coal-water slurry; the oxygen concentration with complete primary combustion would have been 2.1%. Thus, if the primary zone residence time is not adequate to insure almost complete consumption of the available oxygen, the primary fuel will continue to oxidize through much of the reburning zone under oxygen rich conditions. These data emphasize the importance of avoiding significant zone overlap in practical combustion systems. Primary zone residence times of at least 300 ms are clearly desirable.

Figure 5 summarizes similar results on the importance of reburning zone residence time. The data (obtained with propane reburning at two different primary NO_x concentrations) indicate that increasing the rich zone residence time from 140 ms (corresponding to the observed length of the reburning flame) to 400 ms significantly increases the effectiveness of the reburning process at high primary NO_x concentrations but has little effect at low primary NO_x concentrations. Little additional reduction was achieved by extending the reburning residence time beyond 400 ms in either case.

A simplified model was used to simulate the reburning process and assist with the interpretation of the results shown in Fig. 5. The reburning zone was assumed to consist of two parts: a flame zone, lasting 200 ms where half of the primary NO_x was converted to HCN with the rest remaining as NO and a post flame zone where the NO_x and HCN decayed according to the Fenimore mechanism.[18] H_2 and H_2O were assumed to be equilibrated and a fourth order Runge Kutta integration was used to solve the simultaneous differential equations for species concentrations. The empirical correlation based

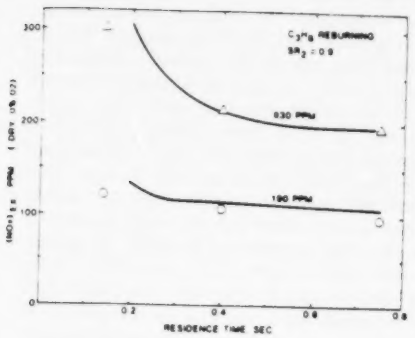

FIG. 3. Influence of Reburning Zone Residence Time: Data and Predictions

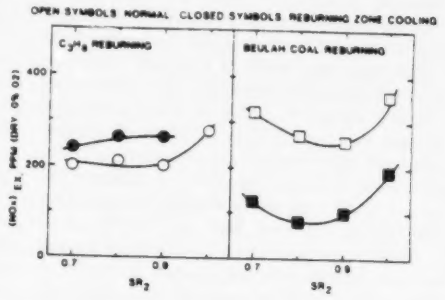

FIG. 6. Impact of Thermal Profile

on the work of Chen and coworkers,[19,20] originally developed to model the formation of NO_x emissions in the final lean stage of a staged coal combustor, was used to approximate the conversion of NH_3, HCN, and NO in the final burnout zone since no validated detailed mechanism currently exists:

$$(NO_x)_{EX} = 0.81 * SR_2^* NO + \frac{0.36[HCN + NH_3]}{1 + 0.0024[HCN + NH_3]} + 53$$

where all concentrations are ppm dry corrected to 0% O_2.

Model predictions are shown as the solid lines in Fig. 5; no adjustments have been made to improve the agreement between the data and model (other than the arbitrary assumption of a 50% NO_x conversion to HCN in the reburning flame zone).

The model agrees reasonably well with the experimental measurements suggesting that, within the temperature and residence time range considered practical for reburning, the Fenimore mechanism and rates are adequate to approximately describe the reactions occurring in the post flame zone. This agrees with the observation of Glass and Wendt[21] who successfully predicted the behavior of NO, NH_3, and HCN in the post flame region of a 2 kg/hr bituminous coal flame using the Fenimore mechanism.

Figure 6 illustrates the impact of thermal history with both gas and coal reburning at $(NO_x)_p$ = 630 ppm. In these experiments cooling coils were added to the lower half of the fuel-rich reburning zone, reducing the temperature at the exit of this zone from 1200 C to 930 C. With propane reburning this resulted in an increase NO_x emissions and detailed measurements indicated that this was directly attributable to an increase in TFN species exiting the fuel rich zone. Reducing the temperature in the fuel rich zone slowed the decay of HCN, NO and NH_3 and this is consistent with previous staged combustion results on gas and liquid fuel firing.[17] Conversely with Beulah coal reburning, adding additional cooling dramatically reduced the exhaust NO_x emissions. Previous work with this coal (a N. Dakota lignite) has indicated that it produces large amounts of NH_3 under fuel-rich conditions[22] and these results suggest that this ammonia is selectively reacting with NO_x in the final burnout zone to produce N_2 and thus reduce NO_x emissions. Chen and coworkers[19] documented a similar effect where in-situ "de-NO_x" as defined by Lyon[23] occurred in the final burnout zone of a heavily cooled staged, coal-fired system. Thus, it is possible to achieve very low emission levels (less than 100 ppm) with coal reburning if the final burnout zone can be practically operated at the conditions required (ca. 1000 C) for selective NO_x reduction by NH_3.

In summary, the system parameter studies indicate that for optimum performance the reburning fuel should be injected after the primary zone combustion is complete ($\tau_1 \geq 300$ ms) and the residence time in the fuel-rich reburning zone (τ_2) should be at least 400 ms. High temperatures favor N_2 formation in the reburning zone, but with solid fuels it is possible to achieve significant additional N_2 formation in the final burnout zone if it can be practically operated at the temperature (ca. 1000 C) required for selective NO_x reduction by NH_3.

Scaling Effects: The Impact of Mixing

The previous sections have focused on chemical (fuel composition) and thermal his-

tory effects; however, for scale up of the reburning technology to be consistently successful, the impacts of finite rate mixing must be quantified. Mixing effects are potentially important because they control: 1) the dispersion of the reburning fuel and, hence, its ability to incinerate primary zone NO_x; 2) the overall conversion of any reburning fuel nitrogen to NO_x; and 3) the oxidation of any gas or solid phase nitrogen species leaving the fuel-rich reburning zone. In full scale systems adequate mixing is difficult to achieve because of the small volumetric flow rates of the reburning fuel (especially with natural gas reburning) and final burnout air and the large distances across which mixing must occur.

Figure 7 summarizes pilot scale data obtained to quantify the importance of reburning fuel mixing. Natural gas was used as the reburning fuel so that the results would represent strictly the influence of fuel dispersion; oxidation of reburning fuel nitrogen was not a factor in these experiments. The results indicate that the effectiveness of the reburning process depends strongly on the dispersion of the reburning fuel. With 700 ppm of primary NO, natural gas reburning only produced a 40% reduction in overall exhaust emissions when the reburning fuel was added as a single axial jet; however, when a line source injector containing 14 holes of 0.3 cm diameter was used to create rapid, complete fuel dispersion, an emission reduction of almost 60% was achieved. An intermediate reduction was achieved with four reburning fuel jets as expected. Similar results were obtained in the small scale testing by switching the reburning fuel injection system from axial to radial injection. Effective incineration of primary zone NO_x can only be achieved if the reburning fuel is widely dispersed prior to its complete oxidation; the NO_x species must contact CH radicals.

Similar small scale testing indicated that effectiveness of the reburning process was relatively insensitive to the mixing of the final burnout air so long as the burnout air was not directed backwards into the fuel-rich NO_x reduction zone (thereby reducing the effective residence time in the rich zone). Large scale testing in the pilot scale furnace as part of this study also confirmed the insensitivity to the rate of burnout air mixing. Tests were conducted with eight opposed 9 cm jets, four 9 cm jets, four 15 cm jets, and one 22 cm jet and the results were essentially indistinguishable.

Figure 8 summarizes the results obtained in the pilot scale furnace with a Utah bituminous coal as both the primary and reburning fuel. These data focus on the complex impact of reburning fuel mixing on both primary zone NO_x incineration and reburning fuel nitrogen oxidation. In these tests the primary zone NO was approximately 350 ppm at $SR_1 = 1.1$ and the reburning fuel was alternately injected through four 7 cm jets and one 22 cm reburning jet. The reburning zone stoichiometry (SR_2) was held constant at 0.9 and the stoichiometry of the reburning fuel jet (oxygen content relative to the combustible material) was varied by using mixture of FGR and air as the transport medium.

When the reburning jet stoichiometry (SR_r) was low (e.g. 0.2) no significant difference was observed between the four jet system (designed to produce more rapid mixing of the reburning fuel with the primary zone exhaust gases) and the single jet. At high reburning jet stoichiometries the single jet system produced significantly lower emissions. These results demonstrate that, with a reburning fuel which contains significant nitrogen, there exists a trade off between high dispersion rates to achieve effective incineration of the primary NO_x and low reburning jet mixing rates to minimize the conversion of reburning fuel nitrogen. Overmoe et al.[24] and Myamae et al.[10] have demon-

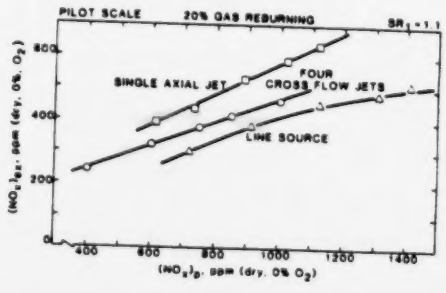

FIG. 7. Importance of Reburning Fuel Mixing—Natural Gas Reburning

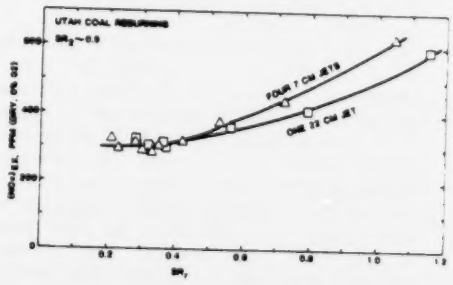

FIG. 8. Influence of Reburning Jet Stoichiometry and Mixing—Coal Reburning

strated that an inert transport medium (e.g. N_2 or FGR) enhances the performance of the reburning process relative to air as the transport medium because the inert medium decreases the conversion of reburning fuel nitrogen. The data shown in Fig. 8 suggest that mixing produces the same trade-off. Thus, in practical systems utilizing a reburning fuel with significant nitrogen, the reburning injection system should be designed to provide rapid dispersion of the reburning fuel but the fuel must be transported with an inert carrier so that the reburning fuel is not oxidized in a large excess of O_2.

Figure 9 illustrates the results of matched bench and pilot scale experiments designed to provide directly comparable scaling data under optimized, commercially acceptable reburning conditions with the Utah bituminous coal as the reburning fuel. The exhaust emissions are shown as a function of the NO_x concentration exiting the primary combustion zone. (In both cases variations in primary NO_x were achieved by doping the natural gas to the main burner with pure NO.) These studies were conducted with a primary zone stoichiometry of 1.1, 20% reburning fuel (SR_2 = 0.9) transported with FGR (SR_r = 0.26), a 300 ms fuel-rich reburning zone and 1430 C at the inlet of the reburning zone. The bench scale tests (25 KW) were conducted with radial reburning fuel and final burnout air injection; the pilot scale tests (3.0 MW) were conducted with four 7.0 cm reburning fuel jets and four 15 cm final burnout air jets both injecting from one wall. In both cases the jets were designed to produce rapid mixing.

Figure 9 demonstrates that a 10^2 scale-up is possible without loss in process effectiveness if the critical stoichiometry, fuel, thermal environment, and reburning fuel dispersion parameters are matched. At normal primary NO_x levels, 20% reburning produced a 50% reduction in the exhaust emissions in agreement with

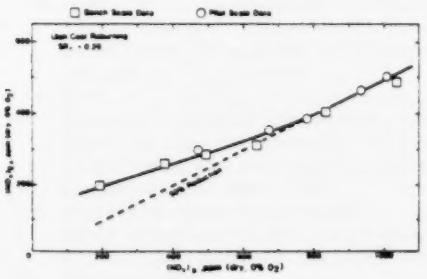

FIG. 9. Comparison of Bench and Pilot Scale Results

previous studies;[4,7] however, at low primary NO levels the percentage reduction decreased due to the oxidation of the reburning fuel nitrogen. The results discussed previously have shown that reburning efficiencies as large as 85% are possible by reducing the burnout zone temperature (e.g. Fig. 6) or reducing SR_1 below 1.1; however, these conditions will not be possible in some commercial applications.

In summary the mixing studies indicate that there exists a trade-off between rapid reburning fuel dispersion to achieve effective incineration of primary zone NO_x and minimization of the contact between the reburning fuel nitrogen and high local oxygen concentrations. If the reburning fuel is natural gas, the fuel injection system should be designed to maximize dispersion; if the reburning fuel contains significant nitrogen, the fuel should be transported with a basically inert medium or dispersion must be retarded.

Conclusions

The results of this study confirm the potential of the reburning process for significant NO_x reductions. Process effectiveness depends strongly upon the stoichiometry, temperature, and residence time in the fuel-rich reburning zone; the NO_x and O_2 concentrations at the end of the primary zone; mixing and stoichiometry of the reburning fuel jet; and the temperature of the final burnout zone. The only reburning fuel parameters which appear to be of first order importance are (1) fuel nitrogen content and (2) the ability of the fuel to form CH fragments. At the optimum reburning stoichiometry (SR_2 = 0.9) the exhaust emissions correlate with the sum of the primary NO_x and the reburning fuel nitrogen. CO and H_2 are significantly less effective than hydrocarbon fuels. Reburning zone residence times of at least 400 ms are desirable and high temperature favor molecular nitrogen formation. Reburning effectiveness decreases with high primary O_2 produced by excessive SR_1, or inadequate primary zone residence time. Rapid mixing of the reburning fuel enhances the effectiveness of the incineration process but it can potentially detract from overall process efficiency with coal reburning due to reburning fuel nitrogen oxidation unless the fuel is transported with an essentially inert gas stream. Extremely low exhaust NO_x levels can be achieved with optimized reburning, low SR_1, and very low final burnout zone temperatures (to produce in-situ de-NO_x).

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COMMENTS

S. Srinivasachar, M.I.T. USA. What fraction of your exit NO_x is due to thermal NO_x in the respective gas flame and coal flame? If it is high, have you considered the possibility that NO_x reduction could be the result of more uniform heat release and lower peak temperatures in the furnace caused by the distributed fuel input?

Author's Reply. In previous studies (17,19) we have shown that the primary source of NO_x emissions with heavy oil and pulverized coal firing is the oxidation of fuel nitrogen; the peak temperatures are simply not sufficient to form large quantities of thermal NO_x.

With natural gas combustion, the thermal NO_x mechanism is the only source of the exhaust emissions and in the gas/gas system reburning certainly does produce some exhaust NO_x reduction due to the distribution of the heat release. However, the overall reduction exceeds that which would have been obtained if the primary load had simply been decreased to the reburning condition value, suggesting that the fuel rich nature of the reburning process is of major importance even in this instance.

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J. O. L. Wendt, University of Arizona, USA. Is it possible and practical to exploit mechanisms of destruction of nitrogenous species in the final burnout (post reburning) zone, in addition to destroying NO in the reburning zone itself?

Author's Reply. Certainly, both processes are clearly significant. Under typical, optimized reburning conditions (NO_x = 630 ppm, SR_2 = 0.9, τ_2 = 400 ms, natural gas reburning) (even without in-situ deNO_x) 70% of the NO is convected to XN species (NH_3, HCN, NO) and 30% directly to N_2 in the reburning zone. When the final burnout air is added 43% of the TFN species (NH_3 + HCN + NO) is convert to N_2 and this corresponds to 30% more of the original NO going to N_2 to produce an overall NO reduction of 60%. The somewhat disappointing aspect of this is that to date we have been unable to significantly improve the XN and N_2 conversion in the final step by altering the burnout air mixing, perhaps because this step is primarily CO combustion.

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N. Arai, Nagoya University, Japan. Could you comment on the most possible reaction for NO-reduction in a reburning zone? This is important in developing successful combustors for any kinds of coal.

Author's Reply. The detailed chemistry of this system is not entirely resolved; however, it appears that the primary reaction for NO reduction is:

$$NO + CH \rightarrow HCN + O.$$

The HCN then decays through $NCO \rightarrow NH \rightarrow N$ and ultimately reaches N_2 via the reverse Zeldovich reaction

$$N + NO \rightarrow N_2 + O.$$

Other alternatives for the primary reaction include:

$$NO + CH_2 \rightarrow HCN + OH, \text{ and}$$

$$NO + C \rightarrow CN + O.$$

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P. C. Malte, University of Washington, USA. Your results with the low-rank coal are very interesting because of the high ammonia concentration and the subsequent thermal de-NO_x process. My concern is the origin of the ammonia. Since vacuum pyrolysis studies show predominant cyano yield from coal, even from low-rank coal, the source of the high ammonia concentration may be the gas-phase reaction. A feature of low-rank coal, compared to bituminous coal, is low organic and tar yield, including low nitrogeneous tar yield. Volatiles from low-rank coal are high in light gases such as CO. Reactions of the HCN or other cyano gases, released from the coal in an environment low in organic species could be the source of the high ammonia concentration. Based on your experience, please comment on this.

Author's Reply. We agree that inert pyrolysis studies (including some conducted by Soloman and coworkers with our lignite coals) have consistently shown HCN to be the predominant XN product. However, we have found NH_3 to greatly exceed HCN at the end of the fuel rich zone with lignite coals and biomass fuels in both this work and previous staged combustion research. Analysis of the hydrocarbons in these systems has shown that HCN yields qualitatively correlate with high hydrocarbon yields (e.g., bituminous coals and heavy oils) while the NH_3 dominated cases do correspond to low hydrocarbon concentrations and higher CO levels as you suggest.

Detailed kinetic modeling suggests that this is due to the rapid destruction of HCN under hot, fuel-rich conditions. The principal reactions appear to be

$$HCN \xrightarrow{OH} HNCO \xrightarrow{H} NH_2$$

followed by either

$$NH_2 + H + M \rightarrow NH_3$$

or

$$NH_2 \xrightarrow{H} NH \xrightarrow{H} N \xrightarrow{NO} N_2$$

$$N \xrightarrow{OH} NO$$

In hydrocarbon rich systems, the HCN may be regenerated by the recycle reaction:

$$NO \xrightarrow{CH} HCN$$

In hydrocarbon deficient environments, repopulation of HCN cannot occur and NH_3 becomes the favored reduced product. Thus, the availability of hydrocarbons is suggested by kinetic analysis to account for the ratioing of the reduced nitrogen between NH_3 and HCN.

●

H. Kremer, Ruhr Universitat, W. Germany. We have performed some limited experiments with German lignite using natural gas as a secondary fuel and operating the first stage at 1000 °C. We could easily get below 100 vppm NO. You have shown that operating the first zone at lower temperatures you get lower NO_x emissions but not below 200 vppm using also lignite as primary fuel. My question is: Did you investigate the influence of temperature more thoroughly than was shown in your figure, and could you give a comment on the results?

Author's Reply. Yes, we investigated temperature more thoroughly; Figure 6 only summarizes two of the key results. We investigated reburning zone temperature over the range of 1560 to 1100 C and burnout zone temperature from 1350 to 870 C. Our results indicate that it is desirable to operate the reducing zone (fuel rich) as hot as possible to maximize XN reduction to N_2 and this is in agreement with previously reported work on liquid fuel flames (England et al., 18th Symposium). We found the exhaust emissions to be relatively insensitive to burnout zone temperature unless it was low enough (Ca 1000 C) to produce in-situ deNO_x reactions (or high enough to cause thermal NO formation). With high primary NO levels typical of lignite or bituminous coal combustion we were only able to reach 100 ppm NO in the exhaust by dropping the final temperature to near 1000 C and inducing in-situ deNO_x with lignite addition. To date we have been unable to produce similar effects with natural gas.

●

C. Lawn, C.E.G.B., U.K. When you say that 50% reduction in NO_x is the 'practical' performance, do you mean that the carbon burn-out does not deteriorate relative to the analyzed condition? Are there any other deleterious effects, such as enhanced slagging in the primary zone?

Author's Reply. Yes, we feel confident that in most practical coal-fired situations we can achieve 50% NO reduction using natural gas reburning without any significant reduction on carbon burnout. We did not specifically examine the impact of reburning on slagging, but no slagging problems were encountered, even in the large pilot scale tests. With certain coals enhanced slagging in the primary could be a concern because although the coal firing rate in the primary would be reduced by 15–20%, it is also desirable to reduce the overall excess O_2 to minimize the amount of reburning fuel required to reach $SR_2 = 0.9$.

●

W. Schreier, L. and G. Steinmueller GmbH, W. Germany.

(1) I'd like to get your comment on the effect of scaling on the stoichiometric ratio. In your experiments good mixing was rather easy to achieve due to the small scale experiments. In a real boiler the dimensions are much larger and mixing becomes a problem. Would you expect a change in the optimum stoichiometry and if so in which direction should it go?

(2) You mentioned during the presentation that the reburning fuel, especially coal, should be injected as inert as possible with respect to NO_x. Do you have any experimental data indicating what this would mean for burnout?

(3) Did you study the effect of particle size of the coal for both primary and secondary fuel on the NO_x-exhaust emission?

Author's Reply.

(1) In the pilot scale experiments we examined effect of SR_2 with slow reburning fuel mixing and found that the optimum stoichiometry shifted from 0.9 to approximately 0.8. Our bench scale data (Fig 2) indicate that the dependence of NO_x on SR_2 with coal reburning (and gas reburning to a lesser extent) is much greater above $SR_2 = 0.9$ than below 0.9. Therefore, if in a boiler it would be desirable to operate slightly richer ($SR_2 < 0.9$) to insure that all regions of the boiler are at slightly fuel rich.

(2) In the pilot scale experiments slightly higher CO emissions were observed with FGR as the transport medium (than with air). However, we don't have the measurements of carbon content in fly ash to quantify the effects of transport medium on burnout.

(3) No, we did not examine the effect of coal particle size in this study. Our previous work (19th symp) suggests that under locally fuel rich conditions decreasing the particle size is beneficial because it enhances fuel nitrogen evolution in an oxygen deficient zone. It also improves carbon burnout.

●

R. Roemer, BASF AG, W. Germany. Can you please make a comment why in the case of coal reburning it is better to use only one jet instead of several jets?

Author's Reply. Optimization of the reburning fuel injector design with coal is complex because of opposing effects. Rapid mixing (several jets) is desirable to insure good incineration of primary NO (via extensive contact with CH radicals); however, rapid mixing of the coal and available O_2 enhances the oxidation of reburning fuel nitrogen, particularly if the coal is transported with air (21% O_2). Figure 8 shows that the optimum approach with coal reburning is to use several injectors to achieve good reburning fuel dispersion but to transport the fuel with an inert carrier so the maximum oxygen concentration that the coal ever experiences is that of the primary exit (1–3%).

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